



Fenton-like oxidation of Reactive Black 5 using rice husk ash based catalyst



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ABSTRACT

Fenton-like oxidation of Reactive Black 5 dye was carried out using iron(III) impregnated on rice husk ash as heterogeneous catalyst. The catalyst was prepared by wet impregnation method and characterized. The effectiveness of this catalyst in degradation and decolorization of the dye, as well as the influence of reaction parameters on the catalytic activity was discussed. The effects of pH, the initial hydrogen peroxide concentration, the catalyst loading, and the temperature on the oxidative degradation and decolorization of Reactive Black 5 have been assessed. The best degradation efficiency (59.71%) and decolorization efficiency (89.18%) was obtained at temperature = 30 °C, pH = 3, $[H_2O_2]_0 = 4$ mM, catalyst loading = 0.5 g/L for initial dye concentration of 100 mg/L.

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1. Introduction

Dye pollutants from textile industries represent one of the major environmental problems. It is estimated that around 15% of the dye is lost during dyeing and finishing processes and is released in wastewaters. The discharge of dye wastewater in the environment is aesthetically undesirable and has serious impact on both environment and human health [1].

Nowadays, various conventional processes are commonly applied for the removal of reactive dyes in contaminated water. However, these methods are usually non-destructive, inefficient, and expensive and in addition resulted in the production of secondary waste products. Therefore, the development of new technologies for the treatment of wastewater containing reactive dye leading to the complete removal of the contaminants now becomes a matter of great concern.

The common alternative is the removal by adsorption. In literature there are several studies aiming at producing new, cheap adsorbent materials to reduce the high cost of the process [2]. In addition, the use of electrochemical oxidation is a further alternative for a successful degradation of [3–5].

Recently, among the emerging treatment approaches, advanced oxidation processes (AOPs) are considered as the most effective and have been proposed as the alternative methods for textile wastewater treatment since they use highly reactive radicals [6].

Among the AOPs, Fenton's reagent is particularly preferable due to its simplicity and the lack of toxicity of the reagents. The term "Fenton's reagent" refers to the mixture of hydrogen peroxide and iron ions. The process can be operated both homogeneously or heterogeneously under various combinations. In the homogeneous phase, chemical reaction is involved only in the degradation process. It should be pointed out that the homogeneous Fenton process has significant disadvantages. The homogeneous Fenton process needs high amounts of iron ions in the solution and the reacted iron ions need to be separated from the system at the end of the reaction, which means an additional removal process [7–9] and iron ions may be deactivated due to complex ion with some iron complexing reagents such as phosphate anions and intermediate oxidation products [10].

To overcome the disadvantages of Fenton type processes, considering the possibility of recovering catalyst, the use of heterogeneous solid Fenton catalysts is recommended. In heterogeneous phase, the physical steps in addition to chemical changes take place on the surface of the catalyst at the active sites where mass transfer limited adsorption of reactant molecules occurs. In other words, physical absorption and desorption in addition to chemical reaction take place. In the process, iron salts, are adsorbed onto the surface of supported catalysts, and the reduction–oxidation reactions between Fe(II)/Fe(III) take place in the presence of hydrogen peroxide which promote the formation of reactive components such as ($\bullet OH$) and ($\bullet OOH$) radicals [1,10].

Recently, many studies are focused on the design and synthesis of environmental friendly catalysts. Selection of environment friendly catalyst should also take into account its reusability, ease of product recovery, low temperature and leaching effect of the metal.

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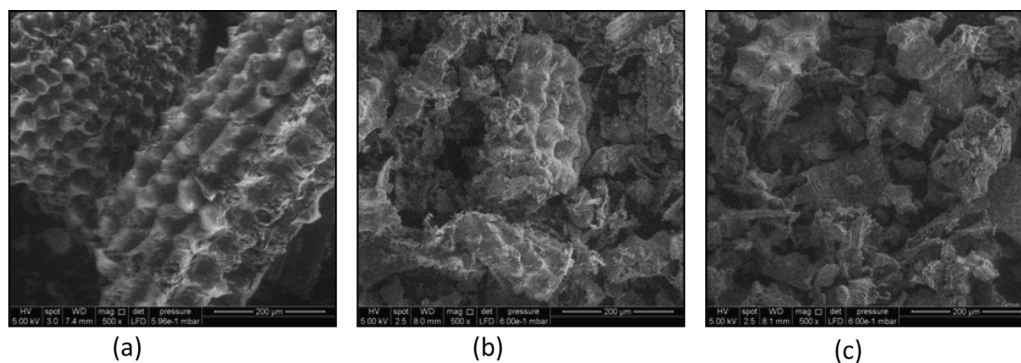


Fig. 1. SEM images of RHA (a), impregnated Fe-RHA (b), Fe-RHA used in the reaction (AR) (c).

Many heterogeneous Fenton-like catalysts have recently been reported as alternative methods, such as iron oxides [9,11,12], and metal immobilized materials [1,13,14]. For example, Soon and Hameed compared the performance of both homogeneous and heterogeneous catalysts. They concluded that the heterogeneous system had ended with better performance for synthetic dye treatment by using a lesser amount of oxidizing agent, wide range of reaction pH, higher catalytic activities and encouraging kinetic rate compared to homogenous catalyst [15].

The use of rice husk-based catalyst for heterogeneous Fenton-like degradation of textile dyes is rarely reported. In particular, Daud and Hameed have reported on the use of a rice husk ash-based (RHA) catalyst for decolorization of Acid Red 1 by Fenton-like process [1] and Gan and Li have studied on Fenton-like degradation of RhB using an iron silica catalyst in which silica was extracted from rice husk [16].

In this regard, in the present paper, the preparation and characterization of an environment friendly catalyst from agricultural waste specifically rice husk ash is presented. Rice husk is the milling byproduct of rice and is a major waste product of the agriculture industry. It is known that the ash has a high specific surface area, high melting point and high porosity and these properties make the ash a valuable raw material for many industries. In addition, it fulfills the requirements for the manufacture of supported-metal catalysts, provided it can maintain its high value of specific surface area [17].

The aim of this study is to assess the catalytic performance of iron(III) immobilized on rice husk ash as heterogeneous catalyst on the Fenton-like oxidation of Reactive Black 5 (RB 5), which is a good model for reactive azo dyes present in textile industry wastewater. This study is an attempt to further advance the use of rice husk which is a major waste product of rice milling industry. Hereby, it is realized to prepare an environmental friendly and low cost catalyst which can be used it in treatment of wastewaters.

2. Experimental

2.1. Catalyst preparation and characterization

2.1.1. Preparation of iron(III) oxide on rice husk ash catalyst

The iron(III) oxide on rice husk ash (RHA) catalyst was prepared by the incipient impregnation method according to the procedure given in literature [18,19].

Rice husk from a local rice mill was washed with distilled water to wash away all the dirt. It was then dried in air for 48 h. The rice husk was then put in a furnace at 600 °C for 5 h. The collected powder was treated with 1.0 M nitric acid for 24 h. It was then filtered and washed thoroughly with deionized water until a constant pH value was obtained. This was labeled as RHA. The RHA was subsequently dried in an oven at 110 °C overnight. Then the iron(III)

oxide was impregnated on rice husk ash (RHA) by the incipient impregnation method.

The catalyst was then characterized. The morphology of the catalysts was observed by means of a Phillips XL30S FEG scanning electron microscope. The characteristics and the surface chemical states of the catalysts were studied using X-ray diffraction analysis operating at 40 kV of voltage and 40 mA of tube current by a Philips X' Pert Pro with Cu K α radiation. The XRD patterns of the solids were recorded in the range of 10–90°. Measurements of specific surface area of the fresh catalyst and the catalyst after used in the reaction were based on the Brunauer–Emmett–Teller (BET) method in a Micromeritics Gemini-2380 apparatus. The weight change of the catalysts was measured using a TGA/DSC 111-Model simultaneous thermal analyzer. The temperature was raised from room temperature to 530 °C using a linear programmer at a heating rate of 10 °C/min. The sample weight was between 10 and 15 mg.

2.2. Experimental set-up

The experimental set-up mainly consisted of a three necked glass reactor, with a volume of 500 mL, a hot plate, a condenser, a thermocouple with digital monitor, and a magnetic stirrer.

2.3. Analysis

The decolorization and degradation efficiencies were used to describe the treatment performance. The decolorization and degradation of RB5 was measured with a UV–vis spectrophotometer (NOVA 400 Merck UV-spectrometer) at 599 and 388 nm. The absorbance at 599 nm is due to the color of the dye solution and it is used to monitor the decolorization of the dye. The absorbance at 388 nm represents the aromatic content of RB5 and the absorbance decrease at 388 nm indicates the degradation of the aromatic part of the dye. The decolorization and degradation efficiencies were calculated using the following equation:

$$\text{Efficiency} = (A_0 - A_t) / A_0,$$

where A_0 is the initial absorbance, A_t is the absorbance at time t .

3. Results and discussion

3.1. Catalyst characterization

The SEM images of RHA, rice husk ash impregnated with Fe, Fe-RHA, and Fe-RHA used in the reaction Fe-RHA(AR) are shown in Fig. 1(a)–(c), respectively. Surface morphology of the RHA was retained after impregnation with iron(III) oxide. The RHA has a porous cellular structure and consists irregular-shaped particles. The basic cellular structure comes from the organic material which RHA is derived and is responsible for the high surface area. If

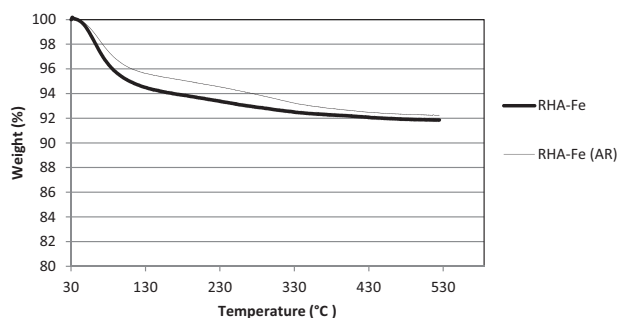


Fig. 2. Results of thermogravimetric analysis.

Fig. 1(b) and (c) are compared, it can be concluded that after reaction, there was a change in both structure and the particle size of the catalyst.

The surface area value corresponding to the fresh catalyst was 208 m²/g. After the reaction, the surface area of the catalyst decreased to 199 m²/g, which represents an insignificant surface area loss of about 4%.

The thermal decomposition behavior was determined by TGA. The TGA results are plotted in Fig. 2. From the figure, it can be clearly seen that there is almost no weight loss in RHA-Fe and RHA-Fe (AR).

X-ray diffraction pattern of RHA and impregnated Fe-RHA are shown in Fig. 3. The pattern of RHA in Fig. 3 contains a peak at 22.5°, which is typical of amorphous silica [20]. No sharp peak was observed in the XRD-spectrograph indicating a good dispersion of iron particles on the support. Gan and Li observed also no sharp peaks in rice husk-based silica supported iron catalyst and they related this by the good dispersion of microcrystalline iron particles on the amorphous silica support in which the microcrystalline particles were too small to diffract X-rays [16].

3.2. Effect of hydrogen peroxide concentration

The effect of H₂O₂ concentration was investigated in a H₂O₂ concentration range between 1 and 16 mM; while keeping the temperature, the catalyst loading and pH constant at 30 °C, 0.5 g/L and 3, respectively. In addition to these an experimental set without addition of H₂O₂ was performed. The results obtained are presented graphically in Figs. 4 and 5.

At very low concentrations of H₂O₂ or in the presence of the catalyst alone in the solution, approximately no degradation or decolorization was observed.

At medium concentration of H₂O₂ (2 mM), the degradation efficiency was very low whereas decolorization was rather higher. For instance at 60 min of reaction there was no degradation, while after

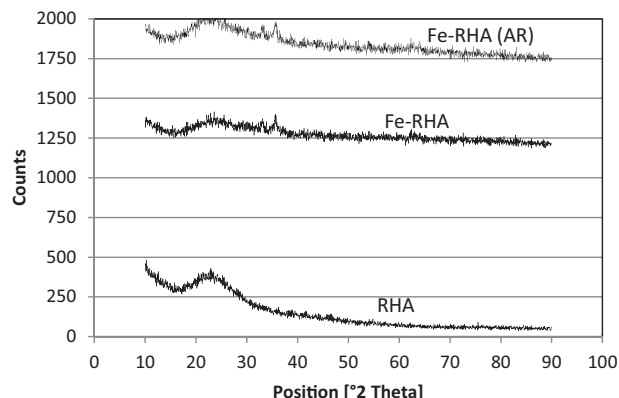


Fig. 3. Results of X-ray diffraction analysis.

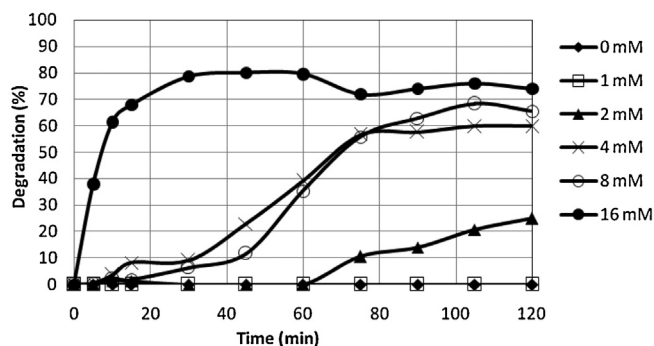


Fig. 4. Effect of H₂O₂ concentration on degradation.

Reaction conditions: catalyst loading: 0.5 g/L, temperature = 30 °C, pH = 3.

60 min, it increased slowly up approximately to 25%. 50% of decolorization efficiency was already achieved in 60 min and reached to 85% at the end of 2 h.

At higher concentrations (4–8 mM), both the degradation and decolorization efficiencies were high. The increase in the decolorization was due to the increase in hydroxyl radical concentration by addition of H₂O₂. But there was no considerable effect in using a concentration of 4 or 8 mM.

At very high concentrations (16 mM), because H₂O₂ generates enough •OH radicals, both the degradation and decolorization proceeded very fast. For example, at 16 mM of H₂O₂ concentration almost 90% decolorization efficiency was achieved within 20 min whereas approximately same decolorization efficiency but in 80 min was achieved with 4 mM of H₂O₂ concentration.

The results indicate that the decolorization and degradation efficiencies and rates increase with increasing H₂O₂ concentration.

Even though H₂O₂ plays an important role, it is recommended to select an optimum H₂O₂ concentration due to the environmental aspects and the cost of H₂O₂ [21–23].

The reason of being an optimum value can be explained as follows: At moderate concentrations, the •OH radicals attack the dye molecules, whereas at high H₂O₂ concentration the scavenging of •OH radicals may occur and hence the degradation may decrease [1,21,24].

Therefore, for the effective degradation and decolorization, 4 mM of H₂O₂ concentration was selected as an optimum concentration.

The results are in agreement with other studies using Fenton treatment for the treatment of azo reactive dyes [1,21–24].

3.3. Effect of temperature

A temperature range of 30–50 °C was studied in order to observe the effect of temperature on the Fenton's treatment at the

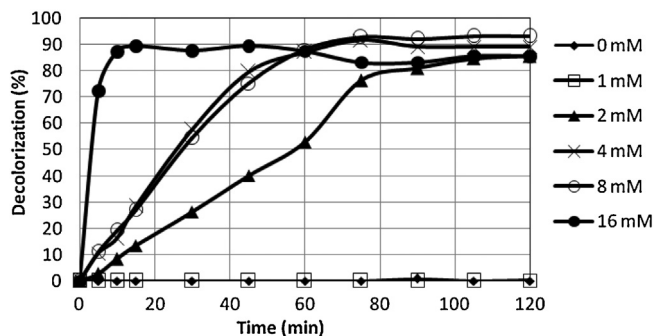


Fig. 5. Effect of H₂O₂ concentration on decolorization.

Reaction conditions: catalyst loading: 0.5 g/L, temperature = 30 °C, pH = 3.

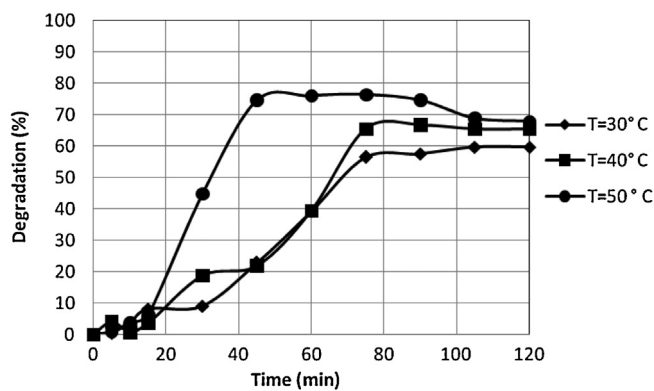


Fig. 6. Effect of temperature on degradation.

Reaction conditions: $[H_2O_2] = 4$ mM, catalyst loading: 0.5 g/L, pH = 3.

concentration of H_2O_2 , the catalyst loading and pH at 4 mM, 0.5 g/L and 3, respectively and the results are shown in Figs. 6 and 7.

The results demonstrate an increase in degradation and decolorization of the dye at the beginning of the reaction with the increase in temperature especially at a temperature of 50°C. In literature, the acceleration of Fenton reaction by temperature is explained by the improvement of generation rate of $\bullet OH$ radical [25,26]. However as the time passes, the difference in the degradation and decolorization rate was not of much evident with respect to temperature changes.

Thus allowing enough time, effective degradation or decolorization can be achieved in the entire temperature range. Hence, as also opposed to many literature reports, 30°C is stated as optimum temperature.

3.4. Effect of catalyst loading

In order to clarify the role of catalyst loading on the degradation and decolorization of RB 5 by Fenton oxidation, a series of experiments were performed with different catalyst loading values from 0.25 to 1 g/L at the fixed concentration of H_2O_2 , the temperature and pH at 4 mM, 30°C and 3, respectively. In addition to these, an experiment in the absence of catalyst was performed. Figs. 8 and 9 show the effect of catalyst loading on the degradation and decolorization. The results indicated that both the degradation and decolorization of the azo dyes are remarkably dependent on the catalyst loading parameter.

In the absence of the catalyst, neither degradation nor decolorization was observed.

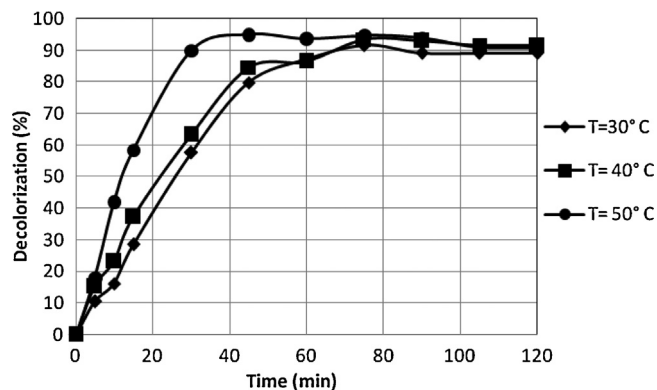


Fig. 7. Effect of temperature on decolorization.

Reaction conditions: $[H_2O_2] = 4$ mM, catalyst loading: 0.5 g/L, pH = 3.

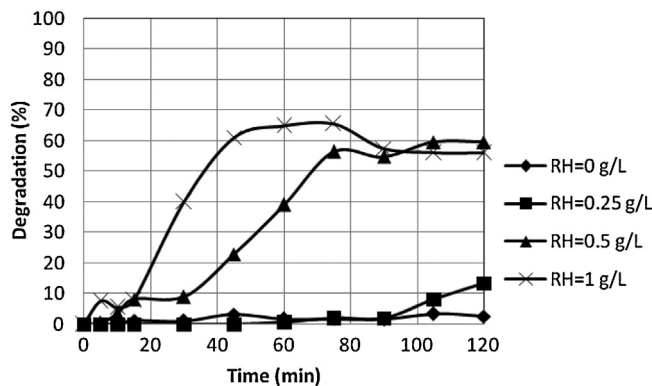


Fig. 8. Effect of catalyst loading on degradation.

Reaction conditions: $[H_2O_2] = 4$ mM, temperature = 30°C, pH = 3.

The low loading value (0.25 g/L) had a minor effect in degradation efficiency, while in decolorization had a more considerable effect. Although the decolorization efficiency was high enough (80%), the rate was rather slow.

Generally, it can be concluded that degradation and decolorization efficiencies and the initial rate increase with increasing catalyst loading but approaches a plateau at higher values. In other words, increasing the catalyst loading above 0.5 g/L did not make a considerable effect. Moreover, many studies have revealed that the use of high catalyst loading (Fe^{2+} concentrations) favors the formation of the $\bullet OH$ radicals, but too high concentration will consume part of the $\bullet OH$ radicals (could lead to the self scavenging of $\bullet OH$ radical by Fe^{2+}) and thus decreases the dye degradation rate [27,28].

Hence, 0.5 g/L catalyst loading was determined to be the optimum value.

3.5. Effect of initial pH

To investigate the effect of initial pH, solutions of RB 5 were treated at various initial pHs (3, 4, 5, 7 and 10) at constant concentration of H_2O_2 , the temperature and catalyst loading at 4 mM, 30°C and 0.5 g/L, respectively.

The results in Figs. 10 and 11 indicate that the degradation and the decolorization efficiencies at the constant operating conditions under both alkaline and weak acidic conditions were very similar and appear to be independent of the initial pH. There was almost no degradation or decolorization.

On the other hand, under strong acidic conditions (pH = 3) there was high degradation and decolorization. This result is in agreement with previous studies in literature [29–32]. Above the optimum pH value, there may be a possible decomposition of H_2O_2

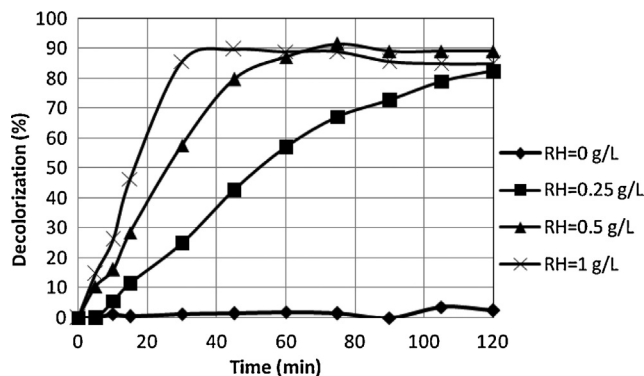


Fig. 9. Effect of catalyst loading on decolorization.

Reaction conditions: $[H_2O_2] = 4$ mM, temperature = 30°C, pH = 3.

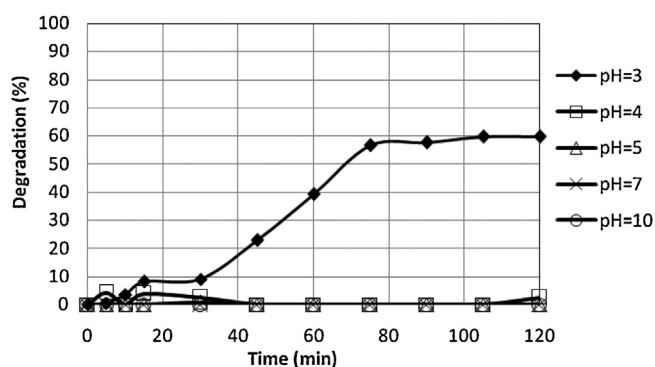


Fig. 10. Effect of initial pH on degradation.

Reaction conditions: $[H_2O_2] = 4$ mM, catalyst loading = 0.5 g/L, temperature = 30 °C.

into water and oxygen and also the possible deactivation of the catalyst with the formation of the other complexes leading to a reduction of $\bullet OH$ radicals [1,33].

3.6. Reusability and leaching of the catalyst

It is important to evaluate the stability and reusability of catalyst for a heterogeneous catalytic system. Thus, reusability and leaching tests were performed during two consecutive runs under determined optimum experimental conditions.

At the end it was found that there is no recordable loss of performance in the two consecutive runs. The highest degradation and decolorization efficiencies with fresh catalyst and the reused catalyst were 59.71%, 89.18%, and 55.62%, 86.10%, respectively.

The metal leaching of catalyst might be important, since continuous leaching of metal ions is one of the direct causes of catalyst deactivation. The catalyst showed good chemical stability since the iron leaching was noticeably low (below the European Union directives of 2 mg/L) for the catalyst [34].

3.7. Comparison of the reported performance of similar heterogeneous catalysts

As mentioned before, the use of rice husk-based catalyst for heterogeneous Fenton-like degradation of textile dyes is rarely reported in literature.

Daud and Hameed have reported on the use of a rice husk ash-based (RHA) catalyst for decolorization of Acid Red 1 by Fenton-like process [1]. BET surface area of the catalyst was measured to be 61.33 m²/g, which is much smaller than the value of the catalyst reported in this study. Decolorization processes led to 96%

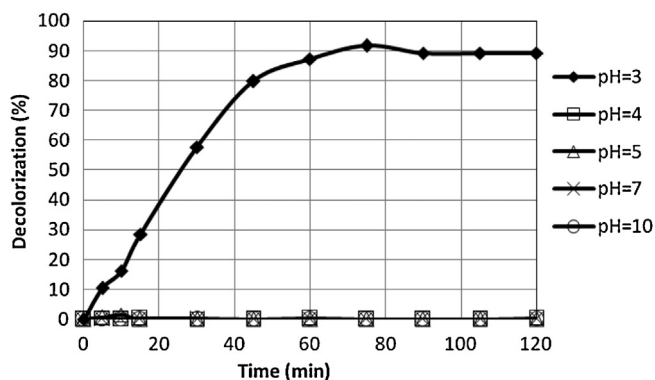


Fig. 11. Effect of initial pH on decolorization.

Reaction conditions: $[H_2O_2] = 4$ mM, catalyst loading = 0.5 g/L, temperature = 30 °C

decolorization of Acid Red 1 within 120 min. They found that the initial activity of the catalyst decreased gradually during successive cycles.

Gan and Li have studied on Fenton-like degradation of Rhodamine B, RhB, using an iron silica catalyst (RHSi-Fe) in which silica was extracted from rice husk [16]. BET surface area of RHSi-Fe was measured to be 422 m²/g, which is higher than the value of the catalyst reported in this study. Almost 100% decolorization was achieved within 10 min at an initial pH of 3.0. They concluded that the catalyst exhibits low iron leaching, good structural stability and no loss of performance in at least three times of repeated use. These results are also in accordance with the results gained in this study.

Generally, if the performance of the prepared catalyst is compared to the similar heterogeneous catalyst used in literature, it can be concluded that the catalyst demonstrates approximately the same decolorization efficiency performance. In some cases the activity of similar catalyst reduction was observed in literature but in this case considerably good stability and reusability of this catalyst was demonstrated.

4. Conclusions

The degradation and decolorization of reactive dye, RB5 in aqueous solutions by Fenton like oxidation using rice husk ash based catalyst (iron(III) impregnated on RHA) have been studied. Based on the results the following conclusions can be drawn:

- The RHA catalyst was prepared by wet impregnation method. The SEM results show that the metal was present, Fe ions were homogeneously distributed and surface morphology of the rice husk did not change after impregnation. Thermal analysis of the catalyst revealed that there was nearly no weight loss. No sharp peak was observed in the XRD-spectrograph indicating a result of good dispersion of iron particles on the support.
- The results showed that with heterogeneous Fenton-like process, 59.71% degradation and 89.18% decolorization can be achieved at the optimized conditions for Reactive Black 5, which are 4 mM H_2O_2 , pH = 3, 30 °C, 0.5 g/L catalyst loading and 75 min reaction time.
- The catalyst showed good chemical stability since the iron leaching was noticeably low.

Generally, it can be concluded that the experimental data demonstrated that the Fenton process is a promising technique for the degradation and decolorization of RB5 dye from aqueous solution.

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